

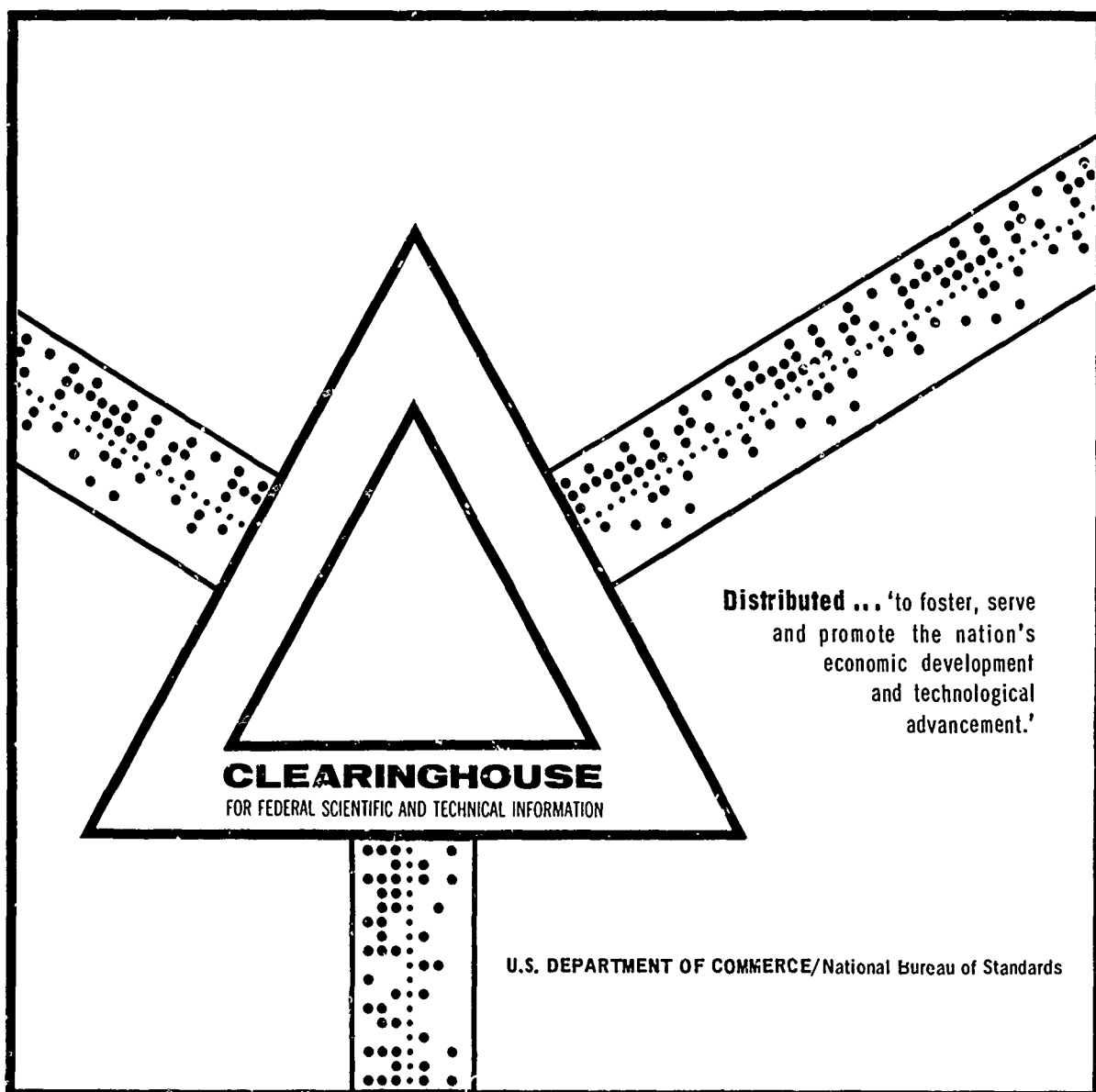
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OXIDATION OF AMMONIA CATALYZED BY MIXED
OXIDES OF COPPER AND CHROMIUM

S. H. Inami, et al

Stanford Research Institute
Menlo Park, California

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MIXED OXIDES OF COPPER AND CHROMIUM*†

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S. H. Inami and H. Wise

SUMMARY

The oxidation of ammonia catalyzed by cupric chromite (CuCr_2O_4) and cuprous chromite ($\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$) has been studied in order to examine the role of the copper ion valence state. The results at 400°C indicate that Cu^{2+} is a much better catalyst for this reaction in which nitrogen is the major product. Similar considerations apply to the complete oxidation of olefinic hydrocarbons. It is suggested that cupric chromite, commonly employed as an ignition and burning-rate catalyst for ammonium perchlorate solid propellants, plays the dual function of catalyzing the decomposition of ammonium perchlorate and the oxidation of ammonia and fuel molecules.

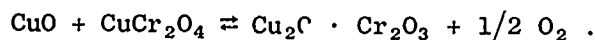
INTRODUCTION

Although the mixed oxides of copper and chromium are employed as promoters of the burning rate and ignition of solid propellants containing ammonium perchlorate (AP), their role in the chemical reaction is not well understood. Since previous studies¹ indicated that in the case of copper chromite oxidation of Cr^{3+} to a higher valence state causes loss of catalytic activity for the AP decomposition, it was of interest to examine the role of the cation valence state of the copper. The studies to be described deal with the catalytic oxidation of ammonia catalyzed by: 1) cupric chromite (CuCr_2O_4), a spinel, and 2) cuprous chromite ($\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$), a mixed oxide compound. The NH_3 - O_2 reaction was chosen because it has been reported that NiO and CuO catalyze the NH_3 oxidation in the gas phase in the absence² and presence³ of AP.

EXPERIMENTAL DETAILS

A. Catalyst Preparation

For the preparation of CuCr_2O_4 , one mole of CuO and two moles of Cr_2O_3 were heated at 870°C in air for 21 hours. The X-ray diffraction analysis indicated that the product was about 50% CuCr_2O_4 . Additional heating at temperature of 1000°C for approximately six hours in a stream of oxygen at one atmosphere yielded a powder which was predominantly CuCr_2O_4 , ~90%. Cuprous chromite $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ was made by heating equal moles of CuCr_2O_4 and CuO in an alumina boat at 1200°C in air for 16 hours.^{4,5} By X-ray analysis the sample was determined to contain > 90% $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$. The formation of $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ proceeds in accordance with the following process:⁶



The purities of the gases used were: $\text{O}_2 > 99.999\%$, $\text{He} > 99.99\%$, and $\text{NH}_3 > 99\%$.

The surface area of the catalysts was evaluated by the BET procedure (Krypton sorption). The surface area of $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ was found to be $0.269 \text{ m}^2/\text{g}$ and that of CuCr_2O_4 $0.412 \text{ m}^2/\text{g}$.

B. Experimental Procedure

The oxidation of ammonia was studied in an apparatus that allowed continuous flow of the oxygen and ammonia mixture over the powdered catalyst (particle size $43\text{-}61\mu$). A weighed mass of catalyst was deposited on a fritted glass disk and contained in a vertical glass cylinder. The flow rates of reactants entering the reactor were metered with calibrated flowmeters. The oxygen partial pressure was kept between 36 and 40 torr while the partial pressure of ammonia was varied. The flow rate of helium diluent gas was adjusted to yield a total flow rate of 230 cc/min . The temperature of the furnace was maintained at 400°C , and the system was operated at a pressure slightly above 1 atmosphere.

At suitable time intervals, the effluent gas mixture was analyzed for N_2 , O_2 , and N_2O by means of gas chromatography. It was necessary to use two columns and two detector circuits to analyze these products. A six-foot Poropak Q column at 75°C was employed to separate N_2O from O_2 and N_2 , while a six-foot column of molecular sieve 5A operated at room temperature was suitable for the separation of O_2 from N_2 .

RESULTS

The experimental results of the heterogeneous oxidation of ammonia with mixed oxide catalysts are presented in Figs. 1 and 2. It will be noted that nitrogen is the predominant nitrogen-containing reaction product. Its specific rate of formation with increasing partial pressure of ammonia (relative to oxygen) appears to follow first-order kinetics. The resulting steady-state nitrogen concentration for a fixed residence time in the reactor is much greater in the case of CuCr_2O_4 than $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ (Fig. 1). For nitrous oxide, the other nitrogen-containing product detected in our measurements, similar considerations

apply. ($N_2 + N_2O$) decreases rapidly with increasing partial pressure of ammonia (Fig. 3), undoubtedly due to the interaction of ammonia with the nitrous oxide. Thus the data suggest that N_2O may be a stable intermediate in the oxidation of ammonia under our experimental conditions.

Pretreatment of the $CuCr_2O_4$ catalyst with ammonia (110 torr, $400^\circ C$), or of the $Cu_2O \cdot Cr_2O_3$ catalyst with oxygen, (760 torr, $400^\circ C$) had little effect on the degree of conversion of reactants or the product distribution. These results point to the kinetic stability of the cation valence states in the mixed oxide catalysts.

The differences observed in the catalytic activity of $CuCr_2O_4$ and $Cu_2O \cdot Cr_2O_3$ for the oxidation of ammonia are also reflected in the oxidation of hydrocarbons such as propylene. At a somewhat lower temperature ($350^\circ C$) we observed the product distribution presented in Table 1. On the basis of these studies with mixed oxides⁷ and additional measurements with oxides of copper,⁸ we concluded that the catalyst containing Cu^{2+} is a far superior catalyst for complete oxidation of the olefin to CO_2 .

As a matter of fact, a commonly used burning-rate catalyst for solid propellants based on AP (Harshaw Cu-0202p) contains an excess of CuO in admixture to $CuCr_2O_4$. On the basis of the results reported, such a material could play the dual function of catalyzing the decomposition of AP and of the oxidation of ammonia and hydrocarbon fuels under the conditions prevailing at the surface of a solid propellant. Our observations further emphasize the important chemical role played by the catalyst in the heterogeneous reactions occurring at the gas/solid interface during propellant ignition and combustion.

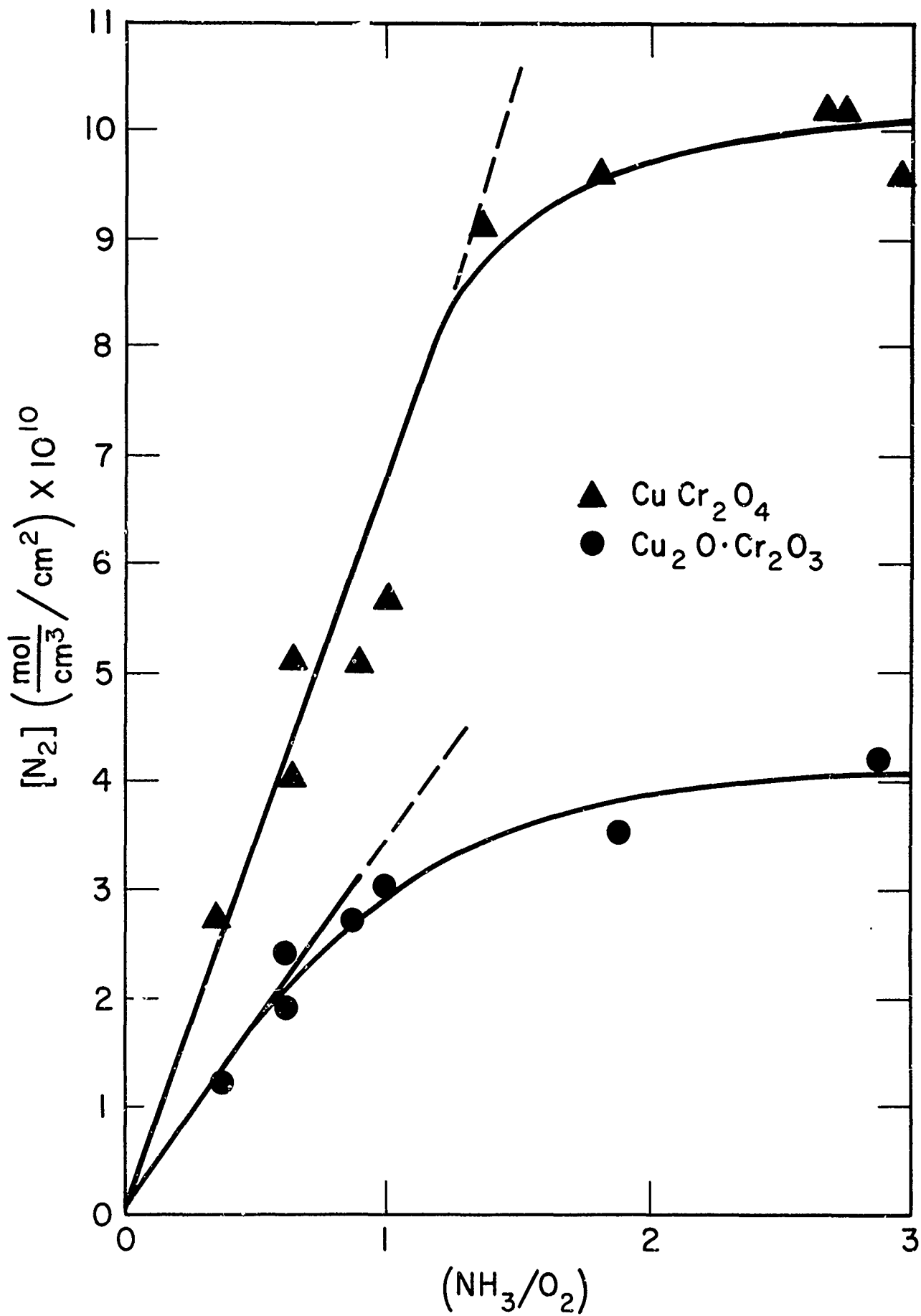
Table 1

Product Distribution from Catalytic Oxidation of Propylene

Catalyst	Conversion (Vol % C ₃ H ₆)	Product (Volume Ratio)
		[CO ₂]/[Other C-Containing Products]
CuCr ₂ O ₄	9	4.9
CuO · Cr ₂ O ₃	13	1.7
None	1	0.1

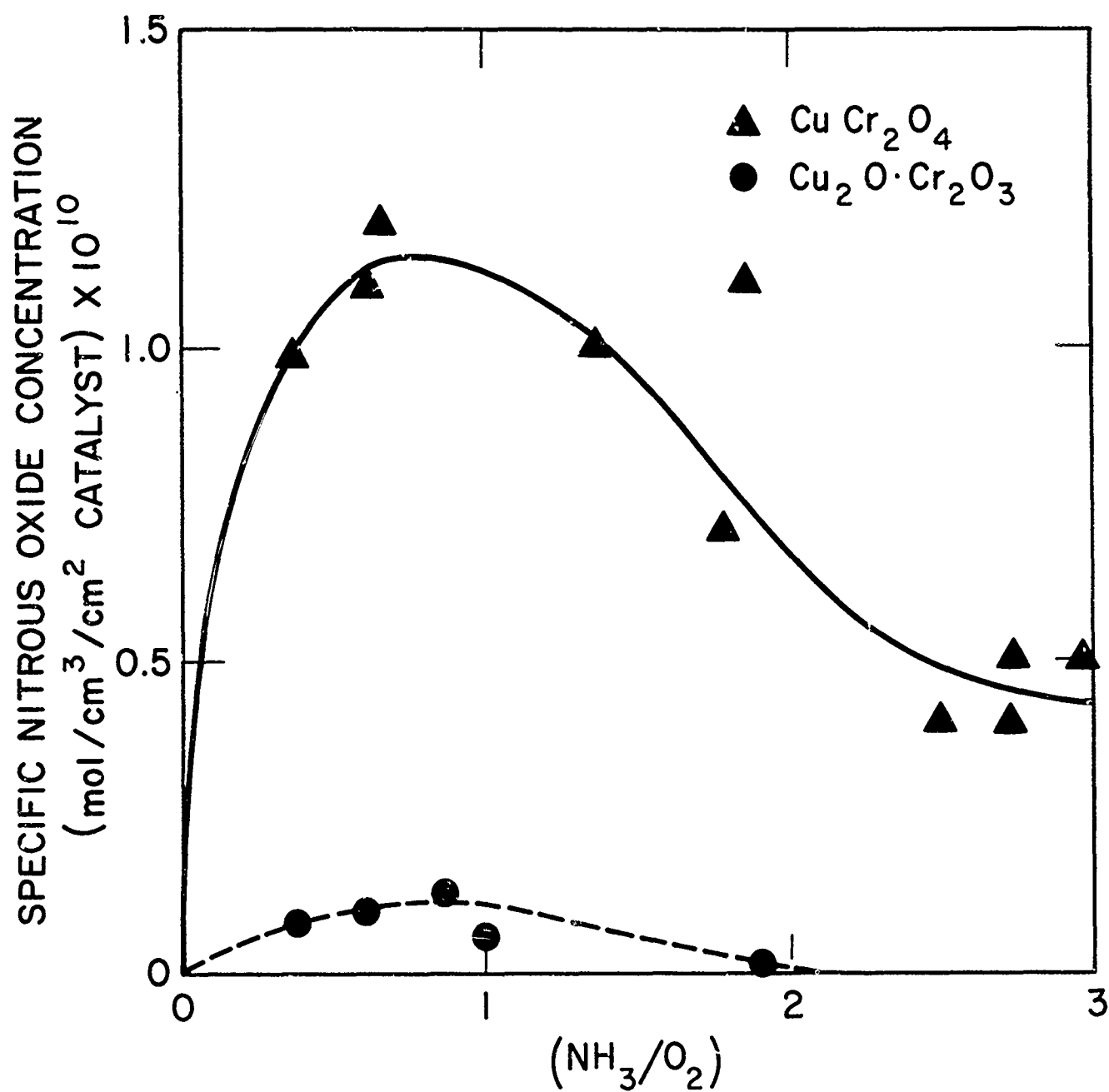
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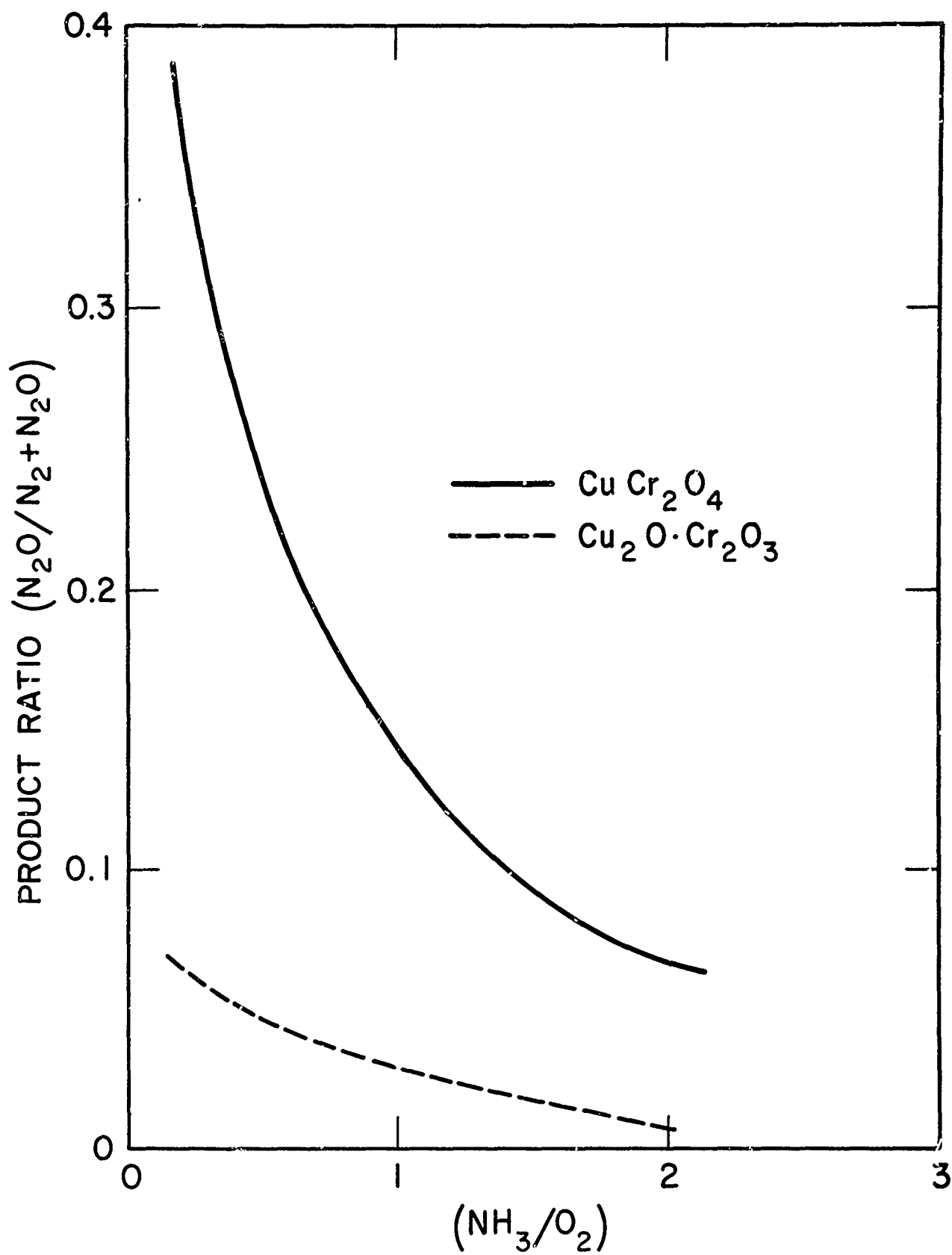
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FIGURE 1 NITROGEN FORMATION AS A FUNCTION OF THE NH_3/O_2 OVER CuCr_2O_4 (▲) AND $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ (●)



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FIGURE 2 NITROUS-OXIDE FORMATION AS A FUNCTION OF THE NH_3/O_2 RATIO OVER CuCr_2O_4 (\blacktriangle) AND $\text{Cu}_2\text{O} \cdot \text{Cr}_2\text{O}_3$ (\bullet)



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FIGURE 3 PRODUCT DISTRIBUTION AS A FUNCTION OF NH_3/O_2 RATIO

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